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The Rapid Precipitation of Metals in the Electrolytic Way.

THESIS.

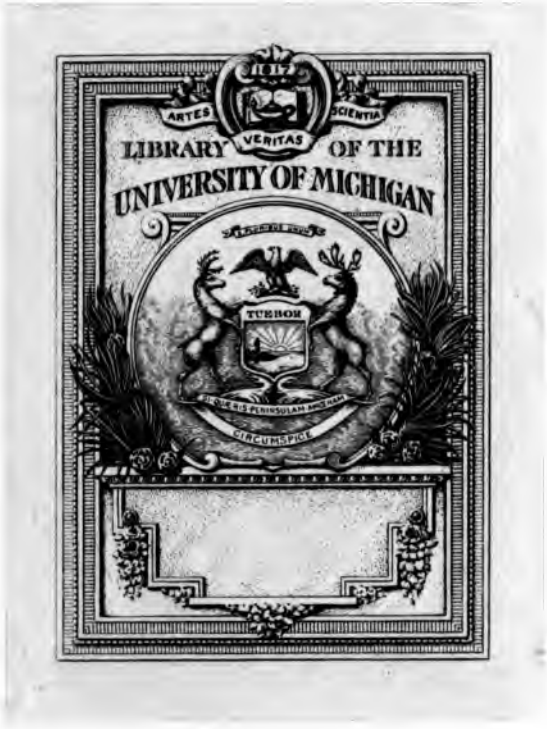
Presented to the Faculty of the Department of Philosophy of the University of Pennsylvania in Partial Fulfilment of the Requirements for the Degree of Doctor of Philosophy,

BY

FRANZ FREDERICK EXNER, A.B.,

Northfield, Minn.

EASTON, PA.
THE CHEMICAL PUBLISHING COMPANY.
1903.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INTRODUCTION.

The publication of books by various authors upon electrochemical analysis, and the rapid increase of laboratories for this kind of work, in institutions of learning, proves that analysis by means of the current has passed its experimental stage. Of recent years laboratories of technical plants, in increasing numbers, have substituted electrolytic methods for cumbersome and time-consuming gravimetric methods. The time factor is a most important one to the technical man, and the time of three to five hours for an electrolytic determination, has no doubt made many slow to exchange their old and tried methods for the new, on the ground that the advantages of the change were not sufficiently pronounced. This investigation, it is believed, will be sufficient to convince the hitherto most skeptical, concerning the advantages of electrolytic analysis, as far as the time factor is concerned. And when we add to this the fact that the necessary apparatus is exceedingly simple, and the operation free from all difficulties, the practical application of the method will commend itself to all.

It has long been recognized that agitation of the electrolyte is advantageous in the deposition of metals. Klobukow[1] calls attention to the fact that from the scientific standpoint the agitation of the electrolyte is very desirable, but on account of mechanical difficulties he could then offer no device for such agitation. Later the same writer[2] described an apparatus designed by himself to produce this agitation. The point that Klobukow lays stress upon is simply the agitation of the liquid, in whatever manner this may be accomplished.

He suggests the blowing of air or other gases into the liquid, but thinks there are certain serious objections to this. He considers that the use of a platinum dish as cathode and a rotating anode is by far the most satisfactory, all things considered. He also modified his apparatus for use as a stirrer, with both electrodes stationary. The motive power used by him was a water motor. The speed of rotation employed for analysis was 120 to 150 revolutions per minute. He concludes his article by stating

[1] J. prakt. Chem., 33, 475.
[2] *Ibid.*, 40, 121.

that the results obtained in electrolysis by means of this apparatus are in many cases astonishing, but he published no results to indicate this work.

Electrical motors for stirring electrolytes have come into considerable use of late years. Various advantages were sought from these rotators, but the idea of using high currents with a high speed of rotation, in order to hasten the deposition has not been advanced until very recently.

Gooch and Medway[1] first published some remarkable results obtained by them by rotating a platinum crucible in the electrolyte, and depositing several metals upon this as the cathode.

An electric motor for rotating the anode has been in use in this laboratory for two years, and has been used for various electrolytic purposes. The following investigation was taken up by the writer, for the purpose of ascertaining what would be the result of using strong currents with a high speed of rotation of the anode.

The rotator used in this investigation was made by the "Electrochemische Werkstätte" at Darmstadt, and is illustrated in Smith's "Electrochemical Analysis," third edition, 1902, page 77. The speed of rotation may vary from 300 to 1700 revolutions per minute. The anode first used was a small stiff spiral, but this was soon replaced by a large spiral. This was made from heavy platinum wire, was two inches in diameter and consisted of six revolutions. The center of the spiral was depressed to give it the form of a shallow bowl. The wire at the end of the spiral was securely fastened to the next inner revolution, and the rigidity of the whole was further secured by binding each revolution into its place with two thin platinum wires running across two perpendicular diameters. It would be advisable to use for this spiral a stout platinum wire alloyed with iridium, because rigidity is essential that the spiral may withstand the strain of rapid rotation in the electrolyte.

Other forms of rotating anode have been proposed, but in this investigation the spiral was found highly satisfactory. The spiral was made bowl-shaped rather than flat, because the electrolyte is whirled against the side of the dish, making a funnel-shaped surface. The surface of the liquid at the center tends to sink below

[1] Am. J. Sci., 15, 320.

the spiral which decreases the surface of contact and thus increases the resistance. The bowl-shaped spiral obviates this difficulty to a great extent. The spiral has the advantage over other forms of anodes with smooth surfaces of circular cross section, because it exerts more friction against the electrolyte and stirs and rotates this more effectively. The cathode used was a platinum dish of 200 cc. capacity. This was covered with two strips of plane glass, fitting closely against each other and against the edge of the dish. The cover glasses were each notched in the middle of the joining edges, making a perforation 5 mm. in diameter when together. Through this the spiral passed.

The amount of liquid in the dish was never more than 125 cc. and not less than 110 cc. The cathode surface is determined with some difficulty, because with different speeds and different electrolytes, the metal is deposited on the dish sometimes up to the very edge, and sometimes it does not come within a centimeter of the edge of the dish. But the depositing surface is approximately 100 sq. cm., and therefore the notation $N.D_{100} = xA$ will express the current conditions with sufficient accuracy for all the work that follows. But it is understood that in each case the current conditions given will be those directly read upon the ammeter and voltmeter.

In all cases in the following work, the electrolyte was first heated nearly to boiling, by placing the platinum dish directly over a full Bunsen flame, before placing it upon the stand for electrolysis. But no external heat was applied during the electrolysis, the high currents used being sufficient to keep the liquid hot, and in most cases at boiling temperature.

The stand used was such as is commonly used in this laboratory, consisting of an iron base supporting an upright glass rod, to which rings are clamped by means of thumb-screws. The ring is connected with one pole of the battery, and supports the dish upon three projecting platinum pegs. The dish with heated electrolyte is set upon the ring and this is raised until the spiral anode of the rotator is immersed in the center of the solution and is then tightly clamped. The other pole of the battery is connected with an arm of the rotator which is in electrical communication with the spiral. (In all cases, excepting lead and manganese, the dish was made

the cathode and the spiral the anode.) The dish is then covered and the rotator started from an incandescent electric light circuit. The battery current is then closed with a switch and the desired current strength obtained by means of a rheostat. When the electrolysis is complete, the rotator is first stopped, then the current is reduced by throwing in resistance from the rheostat. The metal will now be exposed above the surface of the liquid, and it is necessary to fill the dish full with distilled water to cover the metal and prevent its oxidation. The liquid is siphoned off while the dish is kept full by pouring in distilled water from a wash-bottle. The ring is then unclamped and lowered, and the liquid poured off, and the deposit washed with distilled water, dried with alcohol and ether, and weighed.

The question was asked repeatedly in the course of these experiments, "How does the rotation of the anode cause these metals to be precipitated so rapidly?" The explanation that seems most probable to the writer is as follows: In a quiescent liquid the amount of current that can be carried by the electrolyte, is limited by the migration of the ions toward the electrodes, and any mechanical currents which may be produced. If more than the limited amount of current which can be carried by the metallic ions be employed, other ions present will also become carriers, and hydrogen will be liberated with the metal and cause a spongy deposit. But if the liquid be agitated, there will always be an abundance of metallic ions at the cathode to carry even a large current, thus causing a rapid deposition; and if any hydrogen be liberated, the rapid motion of the liquid would quickly detach it from the depositing surface.

Therefore it is not the rotation of the anode or of the cathode that is any advantage in itself, but the agitation of the liquid which is produced by it.

Any other stirrer with fixed electrodes would probably give the same remarkable results.

The speeds of rotation used varied from 300-1,000 revolutions per minute.

Experience taught us that there is nothing gained by increasing the speed indefinitely, and in some cases too great speed is even harmful. The experience of this investigation points to the fol-

lowing as a safe rule: When a given speed of rotation with given current conditions gives a satisfactory metallic deposit, there will be nothing gained by increasing the speed. On the other hand, the increase may be harmful because the solvent action of the electrolyte upon the deposit seems to be increased by increased agitation. In most cases the speed used was 500 to 600 revolutions per minute, but in some cases 300 to 400 produced the best results.

When the higher speeds are used the liquid is thrown up against the cover glasses, but this is not objectionable, because no loss occurs on this account unless the dish is too full. The liquid may sweep around the edge of the dish under the cover glasses throughout the operation without any loss being sustained on this account. But if the electrolyte contains much ammonium salts, or much potassium cyanide, these will creep over the edge of the dish and crystallize on the outside. In this case the liquid must be kept below the edge of the dish, by reducing the speed, or the amount of liquid, or both. There was no difficulty in preventing this creeping in this way in nearly all cases.

Experimental Part.

COPPER.

A solution of copper sulphate was used in each of the following experiments. The speed of rotation was 600 to 700 revolutions per minute. It is understood that in each case, with this metal, as with all the metals treated in this investigation, the solution was first heated nearly to boiling, unless otherwise specified, as explained above. It may also be understood that the dilution in each case was 125 cc.

The electrolytes for this metal were: A. Sulphuric acid; B. Nitric acid; C. Ammonium sulphate and ammonia; D. Ammonium nitrate and ammonia; and E. Potassium cyanide.

A

No. of exp.	$CuSO_4$ = Cu in grams.	H_2SO_4 dil. 1 : 10 in cc.	Current $N.D_{100} = A.$	V.	Time in minutes.[1]	Deposited Cu in grams.	Error in mg.
1	0.4994	1	3	15	3	0.4992	0.2
			4	15	2		
			5	14–9	5		
2	"	1	5	"	5	0.4994	"
3	"	1	5	"	5	0.4994	"

[1] The brace indicates that all those current conditions were used in the experiment acording to the time given.

The deposit from this electrolyte is dark red and rather loose, but sufficiently adherent for washing and weighing. Heating the solution before electrolyzing not only hastens, but greatly improves the deposit. This electrolyte offers a high resistance and makes a large voltage necessary; but the voltage falls as sulphuric acid is liberated by the decomposition.

B.

No. of exp.	$CuSO_4$ = Cu in grams.	Conc. HNO_3. cc.	Conc. NH_4OH sol. cc. After 10 min.	Current $N.D_{100}$ = A.	V.	Time in min.	Deposited Cu in grams.	Error in mg.
1	0.2484	1.0	....	5	10	10	0.2385	—9.9
2	0.2484	1.0	....	5	10	15	0.2387	—9.7
3	0.2484	1.0	....	5	10	20	0.2393	—9.1
4	0.2484	0.5	....	5	12	10	0.2482	—0.2
			5	3	18	5		
5	0.2484	1.0	....	5	10	10	0.2483	—0.1
			5	5	12	5		
6	Identical with 5.							
7	0.4968	1.0	....	5	8	10	0.4964	—0.4
			5	5	10	5		

It seems that under the conditions of Experiments 1, 2 and 3 an equilibrium is reached between the rate of deposition and the solvent action of the electrolyte, and extending the time of action gains nothing. In Experiments 4 to 7 the electrolysis was first conducted for ten minutes in nitric acid solution and then 5 cc. of concentrated ammonia water were added. This causes a change in the resistance of the solution, especially when only 0.5 cc. of nitric acid was used. The change is less marked when 1 cc. of the acid is used, and since it also gives better results, that quantity is to be preferred. The deposit from this electrolyte is dense and bright metallic, and very satisfactory.

C.

No. of exp.	$CuSO_4$ = Cu in grams.	$(NH_4)_2SO_4$ grams.	Conc. NH_4OH in cc.	Current $N.D_{100}$ = A.	V.	Time in minutes.	Deposited Cu in grams.	Error in mg.
1	0.2484	3	20	5	8	5	0.2488	+0.4
2	0.2484	1	20	5	12	5	0.2488	+0.4
3	0.4968	1.5	30	5	12	8	0.4966	—0.2

The conditions of 2 or 3 are preferable. The deposit is dark red and rather loose, but adherent. The slightly high results are probably due to some oxidation during the washing. If

copper estimations are to be made most rapidly, this electrolyte will be preferred.

D.

No. of exp.	$CuSO_4$ = Cu in grams.	NH_4NO_3 in grams.	Conc. NH_4OH solution in cc.	Current $N.D_{100}$ = A.	V.	Time in minutes.	Deposited Cu in grams.	Error in mg.
1	0.2484	3.0	20	5	8	10	0.2463	—2.1
2	0.2484	1.0	20	5	12	10	0.2483	—0.1
3	0.4968	1.5	30	5	12	15	0.4968	0.0
4	0.4968	1.5	30	5	12	14	0.4964	—0.4

The conditions of Experiments 2 and 3 are most desirable. The deposits in these experiments were excellent in character. They were dense and bright metallic, and of a beautiful copper color. Unless the shortest possible time is desired this electrolyte will be preferred to C. Another great advantage of this solution is, that in any ordinary course of analysis the copper is obtained as nitrate. If such a solution with a not too great excess of nitric acid have ammonium sulphate added and ammonia the above conditions will be produced. This was made use of in the separation of copper from nickel.

E.

No. of exp.	$CuSO_4$ = Cu in grams.	KCN.	Current $N.D_{100}$ = A.	V.	Time in min.	Deposited Cu in grams.	Error in mg.
1	0.2484	Least possible for sol.	5	12	10	0.2136	—34.8
2	0.2484	"	6	18	10	0.2465	— 1.9
3	0.2484	"	6	18	18	0.2479	— 0.5
4	0.2484	"	6	18	18	0.2478	— 0.6

This electrolyte yields its last traces of copper very slowly. This is probably due to the solvent action of the solution upon the deposit. A slower speed might have been of advantage. It would also be worth trying to precipitate the copper first with sodium hydrate, then dissolve the precipitate in potassium cyanide. That would give less resistance and less heat. But these deposits were the most beautiful imaginable. They were of a golden red and shone as if they had been polished.

NICKEL.

The solution used in the following experiments was obtained by dissolving pure crystals of the sulphate in water. The speed of rotation was about 600 revolutions per minute. The electro-

lytes tried were: A. Ammonium sulphate and ammonia; B. Acetic acid and ammonia; C. Ammonium nitrate and ammonia; D. Potassium cyanide.

A.

No. of exp.	$NiSO_4$ = Ni in grams.	$(NH_4)_2SO_4$ in grams.	Conc. NH_4OH in cc.	Current $N.D_{100}$ = A.	V.	Time in minutes.	Deposited Ni in grams.	Error in mg.
1	0.2498	1.5	20	4	12	15	0.2496	—0.2
2	0.4996	1.5	30	5	10	15	0.4977	—1.9
3	0.4996	1.5	25	5	10	17	0.4998	+0.2

When more ammonium sulphate was used or less time allowed, the deposit was not complete. The conditions in 1 and 3 are the most desirable. The deposits from this electrolyte are gray in color, but they are dense and adherent, and thoroughly satisfactory.

In a preliminary experiment the nickel sulphate solution was electrolyzed with 2 grams of sodium acetate, but the deposit was wholly on the anode.

B.

No. of exp.	$NiSO_4$ = Ni in grams.	30 % sol. $HC_2H_3O_2$ in cc.	Conc. NH_4OH in cc.	Current $N.D_{100}$ = A.	V.	Time in min.	Deposited Ni in grams.	Error in mg.
1	0.2498	10	10	5	8.0	10	....	....
2	0.2498	10	25	5	6.5	10	0.2498	....

In Experiment 1 the deposit was complete in ten minutes, but there was oxide upon the anode. The conditions in 2 are satisfactory. The deposits are much like those from electrolyte A.

An experiment was performed in which 3 grams of ammonium nitrate were substituted for the acetic acid in experiment B 2; but after ten minutes no deposit had been formed. This suggested a possible separation from copper, which was worked out later. Experiments were also made with potassium cyanide as electrolyte, but only a partial deposit could be obtained, and this electrolyte was abandoned.

Tartaric acid and ammonium tartrate were also tried as electrolytes with this metal, but, although excellent deposits were obtained, these always contained carbon.

ZINC.

For this metal a solution of its sulphate was used. Zinc precipitated directly upon platinum is removed with great difficulty;

and therefore the dish was first coated with silver. The silver and zinc can then be removed together with the utmost ease. The best speed of rotation is 600 to 700 revolutions per minute. The electrolytes used were: A. Sodium acetate and acetic acid; B. Sodium hydrate; C. Sodium hydrate and potassium cyanide.

Preceding each of the following experiments, the dish was silver-coated under the following conditions: 0.25 gram of silver dissolved as nitrate, and 1.5 grams of potassium cyanide diluted to 125 cc. were heated and electrolyzed with a current $N.D_{100} = 1$ A. $V = 4$. The time varied from three to four minutes.

This was sufficient to precipitate nine-tenths of the silver as a dense white deposit, excellent in every way. This was washed, dried and weighed with the dish and the zinc was then deposited upon it.

A.

No. of exp.	$ZnSO_4$ = Zn in grams.	$NaC_2H_3O_2$ in grams.	$HC_2H_3O_2$ 30 per cent. solution in cc.	Current $N.D_{100}$ = A.	V.	Time in minutes.	Deposited Zn in grams.	Error in mg.
1	0.2502	1	0.2	3	18	10	0.2502	..
2	0.2502	3	0.2	4	15	10	0.2502	—0.2
3	0.5004	3	0.2	4	18	15	0.5001	—0.3
4	0.5004	3	0.2	4	10	15	0.5002	—0.2
5	0.5004	1	0.2	4	19	15	0.5000	—0.4

Experiments 1 and 5 show that 1 gram of sodium acetate requires too high a voltage to overcome the resistance, causing an undue amount of heat. The high voltage in Experiment 3 was due to too great speed of rotation. The speed was reduced to about 600 revolutions per minute in Experiment 4. The conditions in Experiments 2 and 4 are to be preferred, and gave very satisfactory results. The deposits were light blue in color, and beautifully crystalline. The crystals were not detached by washing.

B.

No. of exp.	$ZnSO_4$ = Zn in grams.	NaOH in grams.	Current $N.D_{100}$ = A.	V.	Time in min.	Deposited Zn in grams.	Error in mg.
1	0.5004	7	5	5	15	0.5003	—0.1
2	0.5004	5	5	6	15	0.5003	—0.1
3	0.5004	8	5	5	15	0.5004	....
4	0.5004	12	5	5	15	0.5006	+0.2

Bismuth was dissolved in a small excess of nitric acid and electrolyzed with a current $N.D_{100} = 1A$. $V = 2.5$. Time = 18 minutes. The deposited bismuth = 0.5507 gram. The deposit was white and crystalline at first, but later it became black and loose, but was sufficiently adherent for washing and weighing.

Ten different electrolytes were tested with current strengths varying from 4 to 5 A, but all gave worse results than when nitric acid alone was present. There was no difficulty with most of them in obtaining a complete deposition in ten minutes. But the only electrolyte that gave deposits sufficiently satisfactory for analysis was that containing a small excess of nitric acid.

The suggestion of Vortmann was then applied, and the bismuth deposited with mercury as an amalgam. Solutions of mercurous nitrate and bismuth nitrate, each dissolved in the smallest excess of nitric acid, were used.

No. of exp.	$Bi(NO_3)_3$ = Bi in grams.	$HgNO_3$ = Hg in grams.	Conc. HNO_3 in cc.	Current $N.D_{100}$ = A.	V.	Time in min.	Deposited Bi in grams.	Error in mg.
1	0.2970	0.2920	..	4	12	15	0.2965	—0.5
2	0.2970	0.2920	..	4	12	12	0.2967	—0.3
3	0.2970	0.2920	1	5	8.5	8	0.2972	+0.2
4	0.2970	0.2920	1	5	8.5	8	0.2971	+0.1

The 1 cc. of nitric acid which was added, lowered the voltage and also gave better results. The conditions of Experiments 3 and 4 are to be preferred. In each of these experiments the anode was discolored at first, but this coloration dissolved off completely toward the end. The deposit was iron-gray in color and very satisfactory, with the exception that it was difficult to remove the amalgam from the dish with nitric acid. An amount of mercury equal to the weight of bismuth was all that was necessary to produce a satisfactory deposit, but it is probable that if three or four times as much mercury were used the dish would be attacked much less. When mercury was deposited alone, it dissolved off the dish with great ease and did not attack it to any appreciable extent.

MERCURY.

A solution of mercurous nitrate was used, with nitric acid as the electrolyte. The speed of rotation was 700 revolutions per minute.

Nothing is gained by the extra sodium hydrate in Experiment 4. The conditions of Expriment 3 were most satisfactory. The deposit from this electrolyte is not nearly as beautiful as that from electrolyte A, as a portion of it was loose; but it is sufficiently adherent for washing and weighing, and the low voltage will commend itself as an important item in its favor. C. Two experiments were performed in which the zinc sulphate solution was precipitated by sodium hydrate, and the precipitate redissolved in potassium cyanide, and electrolyzed in the usual way. A partial deposit was obtained after fifteen and twenty minutes respectively, in the form of a hard metallic crust. About two-thirds of the entire quantity present was deposited. This electrolyte was abandoned. It may be noted here that the presence of nitric acid or nitrates is fatal to the deposition of zinc, and therefore suggests possible separations. The separation of this metal from copper was accomplished, as will be described later.

SILVER.

The only electrolyte tried for this metal was the cyanide. A solution of silver nitrate was used. A speed of 700 revolutions per minute is preferable. This metal lends itself so readily to this method of determination, that a fuller study of it was deferred and then had to be omitted for lack of time.

No. of exp.	$AgNO_3$ = Ag in grams.	KCN in grams.	Current N.D$_{100}$ = A.	V.	Time in minutes.	Deposited Ag in grams.	Error in mg.
1	0.2495	2	2	5	7	0.2492	+0.2
2	0.4990	2	2	5	10	0.4990	.
3	0.4990	2	2	5	9	0.4992	+0.2

Under these conditions the silver comes down as a dense white deposit, excepting the last traces, which are a little loose, but quite adherent. By using a higher current the time can be shortened, but the deposit will be looser.

BISMUTH.

This metal proved to be one of the most troublesome of the metals, as usual. The speed of rotation employed varied from 700 to 900 revolutions per minute. A single experiment will give the conditions which gave the best deposit of bismuth that could be obtained of this metal alone. Electrolyte: 0.5510 gram of

bismuth was dissolved in a small excess of nitric acid and electrolyzed with a current $N.D_{100} = 1A$. $V = 2.5$. Time = 18 minutes. The deposited bismuth = 0.5507 gram. The deposit was white and crystalline at first, but later it became black and loose, but was sufficiently adherent for washing and weighing.

Ten different electrolytes were tested with current strengths varying from 4 to 5 A, but all gave worse results than when nitric acid alone was present. There was no difficulty with most of them in obtaining a complete deposition in ten minutes. But the only electrolyte that gave deposits sufficiently satisfactory for analysis was that containing a small excess of nitric acid.

The suggestion of Vortmann was then applied, and the bismuth deposited with mercury as an amalgam. Solutions of mercurous nitrate and bismuth nitrate, each dissolved in the smallest excess of nitric acid, were used.

No. of exp.	$Bi(NO_3)_3$ = Bi in grams.	$HgNO_3$ = Hg in grams.	Conc. HNO_3 in cc.	Current $N.D_{100}$ = A.	V.	Time in min.	Deposited Bi in grams.	Error in mg.
1	0.2970	0.2920	..	4	12	15	0.2965	—0.5
2	0.2970	0.2920	..	4	12	12	0.2967	—0.3
3	0.2970	0.2920	1	5	8.5	8	0.2972	+0.2
4	0.2970	0.2920	1	5	8.5	8	0.2971	+0.1

The 1 cc. of nitric acid which was added, lowered the voltage and also gave better results. The conditions of Experiments 3 and 4 are to be preferred. In each of these experiments the anode was discolored at first, but this coloration dissolved off completely toward the end. The deposit was iron-gray in color and very satisfactory, with the exception that it was difficult to remove the amalgam from the dish with nitric acid. An amount of mercury equal to the weight of bismuth was all that was necessary to produce a satisfactory deposit, but it is probable that if three or four times as much mercury were used the dish would be attacked much less. When mercury was deposited alone, it dissolved off the dish with great ease and did not attack it to any appreciable extent.

MERCURY.

A solution of mercurous nitrate was used, with nitric acid as the electrolyte. The speed of rotation was 700 revolutions per minute.

No. of exp.	$HgNO_3$ = Hg in grams.	Conc. HNO_3 in cc.	Current $N.D_{100}$ = A.	V.	Time in minutes.	Deposited Hg in grams.	Error in mg.
1	0.2920	1	4	11	15	0.2920	..
2	0.2920	1	7	12	5	0.2919	—0.1
3	0.5840	1	7	12	7	0.5837	—0.3

These deposits were perfect mirrors of pure mercury, and dissolved off the dish with great ease. The loss in weight of the dish in these three experiments was only 0.6 milligram.

COBALT.

A solution of cobalt sulphate was used. The speed of rotation was 700 revolutions per minute. Two electrolytes were used for this metal: A. Ammonium sulphate and ammonia; B. Sodium and ammonium acetates and ammonia.

A.

No. of exp.	$CoSO_4$ = Co in grams.	$(NH_4)_2SO_4$ in grams.	Conc. NH_4OH sol. in cc.	Current. $N.D_{100}$ = A.	V.	Time in min.	Deposited Co in grams.	Error in mg.
1	0.2460	3	50	5	10	15	0.2433	—2.7
2	0.2460	3	50	5	10	17	0.2440	—2.0

The solution from Experiment 2 gave no test for cobalt with ammonium sulpho-carbonate, but there was a small deposit upon the anode. Further experiments to remedy the defects of this electrolyte were not carried out.

B.

No. of experiment.	$CoSO_4$ = Co in grams.	30 per cent solution $HC_2H_3O_2$ in cc.	$NaC_2H_3O_2$ in grams.	Concentrated NH_4OH in cc.	Current $N.D_{100}$ = A.	V.	Time in minutes.	Deposited Co in grams.	Error in milligrams
1	0.2460	10	.	60	5	8	16	0.2404	5.6
2	0.2460	5	5	60	5	12 to 8	15	0.2462	+0.2
3	0.2460	.	2	60	5	15 to 12	15	0.2462	+0.2
4	0.2460	5	1	50	5	12 to 9	17	0.2459	—0.1
5	0.2460	5	1	50	5	10 to 7	15	0.2459	—0.1
6	0.4920	5	1	50	5	9 to 8	22	0.4916	—0.4
7	0.4920	5	1	50	5	9 to 8	22	9.4917	—0.3

In Experiment 1 the deposit was of excellent quality, but it was incomplete and there was oxide on the anode.

In Experiment 2 the deposit was very good and there was but a slight discoloration of the anode.

In Experiment 3 the deposit was satisfactory, but not as good as in 2. There was nothing on the anode.

The deposits in Experiments 4 to 7 were good, of gray metallic character, and the discoloration of the anode was so slight as to be negligible. The high voltage in Experiments 2, 3 and 4 was due to too great speed of rotation, causing insufficient contact between liquid and anode.

In the last three experiments the speed was reduced to 500 revolutions per minute and was preferable. The conditions employed in these are to be recommended. When the electrolyte is heated directly over the flame some basic compound may separate on the surface. In that case the liquid is best heated while agitated. It seems that the sodium acetate hastens the deposit and prevents deposition upon the anode, while the ammonium acetate improves the deposit, but retards its formation. The proportions of the two as given above seemed to give the best results.

CADMIUM.

A solution of cadmium nitrate was first prepared and tested with various electrolytes, with the following results: Cadmium nitrate and nitric acid gave no deposit. With sodium acetate also it gave no deposit. With potassium cyanide it was deposited without rotation, but when the rotator was started the deposit at once dissolved again. This was a very good illustration of the increased solvent action of the electrolyte when it is agitated. Cadmium nitrate precipitated with sodium hydrate and the precipitate dissolved with potassium cyanide, gave a slight crystalline deposit, but it was incomplete. Therefore nitric acid and nitrates must be avoided when cadmium is to be deposited. This again suggests the possibility of separations. A solution of cadmium sulphate was then prepared and the following electrolytes used with it: A. Sulphuric acid; B. Sodium acetate and potassium sulphate; C. Potassium cyanide. The speed of rotation was about 600 revolutions per minute.

				A.			
No. of exp.	$CdSO_4$ = Cd in grams.	H_2SO_4 dil. 1 : 10 in cc.	Current $N.D_{100}$ = A.	V.	Time in min.	Deposited Cd in grams.	Error in mg.
1	0.2756	3	5	9	10	0.2756	....
2	0.2756	1	5	17–11	10	0.2755	—0.1
3	0.5512	1	5	8	15	0.5508	—0.4

Deposit 1 was crystalline at first, but the last came down loose, but sufficiently adherent. In Experiment 2 the voltage was high at first, but fell as the sulphuric acid was liberated in the electrolysis. Deposits 2 and 3 were beautifully crystalline and very satisfactory.

B. Experiment 1. Electrolyte: Cd = 0.5512 gram. Sodium acetate = 2 grams. Potassium sulphate = 0.5 gram. Current $N.D_{100} = 5$ A. V = 12. Time = 15 minutes. The deposited cadmium weighed 0.5514 gram. The potassium sulphate was necessary to increase the conductivity of the electrolyte. The voltage was 18 before this salt was added. There was some tendency to creeping.

Experiment 2. Electrolyte: Cd = 0.5512 gram. Precipitated with 0.5 gram of sodium hydrate, precipitate dissolved with acetic acid, and 0.5 gram of potassium sulphate added. Current $N.D_{100} = 5$ A. V = 11. Time = 15 minutes Deposited Cd = 0.5514 gram. There was no creeping. The deposits in 1 and 2 were crystalline and satisfactory, but not quite as good as those from sulphuric acid.

C.

No. of exp.	$CdSO_4$ = Cd in grams.	NaOH in grams.	KCN in grams.	Current $N.D_{100}$ = A.	V.	Time in min.	Deposited Cd in grams.	Error in mg.
1	0.5530	5	2	5	8	15	0.5531	+0.1
2	0.5530	5	2	5	8	10	0.5528	—0.2
3	0.5530	5	2	5	8	12	0.5528	—0.2
4	0.5530	5	2	5	8	10	0.5530	....

The deposits were white and compact and very satisfactory. An experiment was tried in which the cyanide was added without the sodium hydrate, but the deposit was not good, the last being loose and gray in color, and weighing too heavy. When it was dissolved it showed carbon. The attempt was also made to shorten the time by increasing the current, but without success.

IRON.

A solution of ferric ammonium sulphate with ammonium oxalate was used as electrolyte. The speed of rotation was about 800 revolutions per minute.

No. of exp.	Ferric am. alum= Fe in grams.	$(NH_4)_2C_2O_4$ in grams.	$H_2C_2O_4$ sat. sol. in cc.	Current $N.D_{100}$=A.	V.	Time in minutes.	Deposited Fe in grams.	Error in mg.
1	0.2461	7	1	7	7.4	25	0.2458	—0.3
2	0.2461	7.5	·	7	7.5	25	0.2463	+0.2
3	0.2461	7.5	·	7	7.5	25	0.2461	..
4	0.4922	7.5	·	7	7.5	35	0.4922	..

The ammonium oxalate was added in the form of a hot saturated solution. This was necessary in order to keep the liquid from exceeding 125 cc. 5 grams of oxalate were insufficient, and when only 3 grams were used the deposit was incomplete and very inferior. The best results were obtained with 7.5 grams of the oxalate. These experiments seem to show that the oxalic acid is unnecessary and the best results are obtained without it. There was at no time an indication of the separation of a basic salt in the solution, though this developed a strong odor of ammonia. The only place where a slight separation of basic iron occurred was on the cover glasses toward the last. These were rinsed off with oxalic acid. There was a strong tendency to creeping because of the ammonium salts, and this required a good deal of manipulation to avoid appreciable loss. But it is probable that a slower speed of rotation might have been used, and the creeping wholly prevented.. Aside from the creeping, the method seemed like an ideal determination of iron. The deposits were so dense and white that they resembled the polished platinum dish. The less oxalic acid was used the smaller was the amount of carbon contaminating the deposit. In the last three experiments it was scarcely perceptible.

LEAD.

This metal, as is customary, was deposited upon the anode as dioxide. The connections were therefore changed so as to make the dish the anode and the spiral the cathode. The deposit tended to loosen from a smooth dish, and therefore a dish which had its inner surface roughened by a sand blast, was used. Upon this the deposit adhered perfectly. Over a gram of deposited dioxide showed no tendency to scale off. The speed of rotation used was about 600 revolutions per minute. The deposit, after washing and drying with alcohol and ether, was dried in an air-bath at 180° C. to constant weight, and weighed as dioxide. The only electrolyte used was nitric acid.

No. of exp.	$Pb(NO_3)_2$ = Pb in grams.	HNO_3 conc. in cc.	Current $N.D_{100}$ = A.	V.	Time in min.	Deposited PbO_2 in grams.	Error in mg.
1	0.2807	20	10	4.5	10	0.2804	—0.3
2	0.2807	20	10	4.5	10	0.2804	—0.3
3	0.5614	20	10	4.5	13	0.5613	—0.1
4	0.5614	20	10	4.5	13	0.5614	....
5	1.1228	20	10	4.5	15	1.1228	....

The deposits of lead dioxide were of a fine, uniform velvety black color. Such a large amount of nitric acid makes an electrolyte of very low resistance, and permits a large amperage without the production of too much heat. When less nitric acid was used there was some deposition upon the cathode, but with 20 cc. present this did not occur at all.

MANGANESE.

This element offered a great deal of difficulty, and was finally abandoned. The most serious obstacle lay in the fact that the hydrated peroxide, which was deposited upon the dish as the anode, scaled off from the roughened dish, and being churned up in the electrolyte, was partially redissolved, so that the deposition was hardly ever complete. Various electrolytes and expedients were tried, but none proved successful. If some means can be devised for making the deposit adhere, this element will be deposited by this method with great ease.

MOLYBDENUM.

This metal is deposited upon the cathode as a hydrated sesquioxide. This is of a velvet-black color, and iridescent in thin films. This deposit cannot be weighed satisfactorily, and is therefore dissolved from off the dish with nitric acid. The solution is evaporated to dryness on the water-bath and gently heated over a flame. A low speed of about 300 to 400 revolutions per minute is preferable in order to prevent creeping over the edge of the dish. The conditions which gave excellent results were as follows:

Electrolyte: A solution of sodium molybdate containing 0.2250 gram of MoO_3 was placed in the dish, and to this were added 2 cc. of sulphuric acid (dilute 1 : 10), and 1 gram of potassium sulphate. The current $N.D_{100} = 4$ A. V = 15. Time = 20 minutes. The found MoO_3 = 0.2246 gram. The solution siphoned off was

tested with pure hydrochloric acid, ammonium sulpho-cyanate and zinc, but no evidence for molybdenum appeared. It was attempted to deposit larger amounts, but without success, because when more than the above amount is used the deposit scaled off, and was partly redissolved, thus making complete deposition impossible.

TIN.

The compound of tin used was a freshly prepared solution of stannous ammonium chloride. The speed of rotation is an important matter with this metal. A speed of 600 to 700 revolutions per minute was used at first, but this produced serious creeping of the ammonium salts, to the outside of the dish. The speed was then changed to about 300 revolutions per minute. This kept the liquid below the edge of the dish and controlled the creeping fairly well.

No. of exp.	$SnCl_2$. $2NH_4Cl$ = Sn in grams.	$(NH_4)_2C_2O_4$ hot sat. sol. in cc.	Current $N.D_{100}$=A.	V.	Time in minutes.	Deposited Sn in grams.	Error in mg.
1	0.5396	100	5	5	13	0.5392	—0.4
2	0.2193	100	5	5.5	15	0.2193	....
3	0.2193	100	5	5.5	15	0.2191	—0.2
4	0.2193	100	5	5.5	15	0.2191	—0.2
5	0.2193	100	5	5.5	15	0.2193	....
6	0.4355	100	5 / 8	5.5 / 6.5	15[1] / 3	0.4353	—0.2
7	0.4355	100	5 / 8	5.5 / 6.5	15 / 5	0.4355	....
8	1.0800	100	5	4.5	20	1.0801	+0.1

The above table does not represent all the experiments performed, but it does represent all performed under these conditions.

A number of determinations were made in which oxalic acid was added in varying amounts, either at the beginning or from time to time. This retarded the deposit and also caused a greater contamination of the metal by carbon. A number of experiments were made in which it was attempted to reduce the time; but it was always noticed that when the liquid was poured off it was milky. This milkiness did not disappear if the solution was

[1] In Experiments 6 and 7 the brace indicates two current conditions. The 5-A current running 15 minutes after which it was changed to 8-A.

strongly acidified with hydrochloric acid, unless heated for some time with it. Whenever this milkiness appeared the deposit would weigh too light. Addition of oxalic acid did not prevent the formation of this basic compound. Nevertheless, if the current was allowed to act long enough the milkiness disappeared, the deposit weighed correctly, and no trace of tin could be detected in the solution. Therefore, if the conditions given in the table be followed and a milkiness appears when the liquid is poured off, more time alone is necessary to remedy the defect.

Some experiments were also made upon a cold solution and some upon a solution which was gently warmed, but the results were inferior to those in which the solution was heated to boiling. The character of the deposit is silver-white at first, but the latter part of the deposit is somewhat loose, yet satisfactory for analytical purposes. As was said above, a slow speed that will reduce the tendency to creeping to a minimum is necessary.

GOLD.

The solution used was gold chloride. The electrolyte was potassium cyanide. The speed of rotation was about 500 revolutions per minute.

No. of exp.	$AuCl_3$ = Au in grams.	KCN in grams.	Current $N.D_{100}$ = A.	V.	Time in min.	Deposited Au in grams.	Error in mg.
1	0.029	1.0	5	11	10	0.0289	0.1
2	0.0725	2.0	5	11	10	0.0725	..
3	0.1450	1.5	5	11	7	0.1447	—0.3

The deposits were most excellent.

ANTIMONY.

The antimony solution used was the chloride with just enough hydrochloric acid to keep it in solution. 100 cubic centimeters of the solution contained about 3 grams of metal. The only satisfactory electrolyte found was a mixture of sodium hydrate, sodium hydrogen sulphide and potassium cyanide. The sulphide solution was freshly prepared by saturating a 10 per cent. solution of sodium hydrate with hydrogen sulphide. The best speed of rotation was 400 to 500 revolutions per minute.

No. of exp.	$SbCl_3$ + HCl = Sb in grams.	NaOH 10% sol. in cc.	NaHS in cc.	KCN in grams.	Current N.D.$_{100}$ = A.	V.	Time in min.	Deposited Sb in grams.	Error in mg.
1	0.3042	30	20	2	5	4.5	20	0.3042	....
2	0.3042	30	20	2	5	4.5	20	0.3041	—0.1
3	0.3042	30	20	2	5	4.5	18	0.3041	—0.1

The deposits under these conditions are most excellent. They are dense, bright metallic and complete. Experiments in which it was attempted to reduce the time with the above conditions, proved unsuccessful.

These deposits are removed from the dish with ease by a warm mixture of nitric and tartaric acids.

The amount of the above deposits represents the limit under those conditions. Even with this there was a slight tendency on the part of the hard coating to crack and scale off. With larger amounts the defect is serious. With smaller amounts that does not happen at all. The antimony solution was first introduced into the dish, then the sodium hydrate was added and the mixture stirred and warmed until all the precipitate had dissolved, after which the sulphide and cyanide were added. In the first experiments with this metal, sodium sulphide alone was used as electrolyte. The deposit each time was like a polished black mirror, but it was never complete. When the solution from the deposit was treated with hydrochloric acid, a precipitate always resulted.

The more sulphide was used the more incomplete did the deposit become. When 100 cc. of sulphide were used for 0.25 gram of antimony, nothing was deposited during the first fifteen minutes.

Then the antimony solution was precipitated and redissolved with sodium hydrate and electrolyzed. The antimony was deposited quickly, but it was black and spongy. The antimony solution was then precipitated and redissolved with sodium hydrate, 20 cc. of sodium sulphide added, and the mixture electrolyzed. This deposit was nearly all white, but it was still incomplete after twenty minutes' action of the current. In the next experiments potassium cyanide was added, with the thought that the cyanide should take up the sulphur and thus prevent the formation of polysulphides. This proved effective and gave the series of results given above.

ARSENIC.

Numerous experiments were performed to obtain arsenic in the form of an amalgam according to Vortmann's suggestion. The trioxide was oxidized and dissolved in nitric acid, and this solution electrolyzed with mercurous nitrate. The thought was that in the presence of considerable nitric acid the arsenic could not escape as arsine. The mercury was deposited and some arsenic was deposited on the top of it in the form of a black mud, but a portion was always volatilized, and in one case the escape was complete. Under these conditions the two elements did not amalgamate at all.

SEPARATIONS.

SEPARATION OF COPPER FROM NICKEL.

The sulphate solutions of both metals were used. The speed of rotation was about 600 revolutions per minute.

No. of experiment.	$CuSO_4$ = Cu in grams.	$NiSO_4$ = Ni in grams.	Concentrated HNO_3 in cc.	NH_4NO_3 in grams.	Current $N.D_{100}$=A.	V.	Time in minutes.	Deposited Cu in grams.	Error in milligrams.
1	0.2457	0.25	0.25	3	4	5	15	0.2460	+0.3
2	0.2457	0.25	0.25	3	4	5	15	0.2458	+0.1

The deposits of copper were excellent, free from nickel and complete. Several other experiments were performed in which more free nitric acid was used, and some in which less time was allowed, but in all these the deposit was incomplete. The least possible free nitric acid must be used, because of its solvent action on the deposit, which prevents the last traces from being precipitated. The separation is probably possible also in the ammonia solution in the presence of about 3 grams of ammonium nitrate.

Analysis 1 of Nickel Coin.

A nickel coin weighing 4.8514 grams was dissolved in nitric acid, evaporated on the water-bath, and the crystallized residue dissolved in water, and the solution diluted in a 250 cc. flask to the mark. Twenty-five cubic centimeters of this solution were placed in a weighed platinum dish and 3 grams of ammonium sulphate, and 1 gram of ammonium nitrate were added. This was diluted